

PATENT SPECIFICATION

680,605



Date of Application and filing Complete Specification March 9, 1951.

No. 5763/51.

Application made in United States of America on May 9, 1950.

Complete Specification Published Oct. 8, 1952.

Index at acceptance :—Class 2(iii), B1d.

COMPLETE SPECIFICATION

Phosphoric Acid Polymerization of Olefins

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organised under the laws of the State of Delaware, United States of America, and having offices at 200, Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polymers from normally gaseous olefin hydrocarbons by means of a polymerization process employing a phosphoric acid film catalyst. In particular, the invention relates to improvements in the polymerization processes employing as the catalyst a film of phosphoric acid adsorbed upon an inert, non-porous support.

It has been previously recognized and commercially accepted that phosphoric acid catalyzes the polymerization of normally gaseous olefin hydrocarbons to produce liquid polymers of substantial value as anti-knock constituents of motor fuels and gasoline blending components. The types of polymerization processes utilizing phosphoric acid as the catalytic agent may be divided into two classifications: (1) processes employing a so-called "solid phosphoric acid catalyst" which bears reference to a pelleted or extruded catalyst consisting of an inert porous clay-type of support impregnated with phosphoric acid such as phosphoric acid-impregnated kieselguhr; and (2) processes using the so-called "film acid catalyst" which consists of a film of phosphoric acid adsorbed upon an inert, non-porous type of support, as represented by phosphoric acid adsorbed on quartz chips.

The polymerization reaction is highly exothermic and must be closely controlled to prevent undesirable polymer formation and decomposition of product into

coke and other carbonaceous matter. In addition, the phosphoric acid catalysts, and particularly the impregnated porous catalysts, are very susceptible to excessive temperature changes in this reaction which results in marked changes in catalytic activity and, in the case of the so-called "solid catalyst", in a physical deterioration of the catalyst support structure.

Various methods of temperature control have heretofore been proposed and applied to the polymerization process. In the main, all of the operable proposals involve the use of an inert diluent or heat exchange medium, such as the saturated hydrocarbons obtained as stabilizer overhead, which is blended with the reactive feed and/or injected into the reactor between the spaced catalyst beds. Effective temperature control is only attained by the use of sufficient inert diluent to reduce the olefin content of the total reactor charge to a point where the heat capacity of the reaction mixture is sufficient to absorb the heat of reaction without excessive temperature rise. This naturally requires a reduction of olefin concentration of the feed and places a maximum allowable olefin concentration in the total reactor feed for a given temperature rise through the reactor. Heretofore, it has been practically unfeasible to operate this type of polymerization process with a total reactor charge containing greater than 35% olefin concentration when charging a C_3 — C_4 olefin feed, irrespective of the particular method of temperature control employed.

According to the present invention it has been found that a marked improvement in the efficiency and conduct of the film-acid process is attained by the injection of cold, reactive olefin feed at a plurality of intermediate positions within the catalyst bed. Although the primary effect of this feature is a more efficient method of temperature control throughout the reaction zone, additional

[Price 2/8]

Price 2/8

BEST AVAILABLE COPY

significant improvements are obtained which are coincident with the use of the film-acid type of catalyst.

5 In its general perspective, the present process is adapted to the polymerization of low-boiling or normally gaseous olefin hydrocarbons to produce selective liquid polymers ranging from the dimers through the tetramers. The olefin feed is
10 conventionally water-washed to remove any traces of deleterious nitrogen compounds and is brought up to the desired reaction pressure. The pressurized stream is divided by a proportioning means into a feed stream and a quench stream. The
15 feed stream is passed through a preheater or heat exchanger to raise the temperature to the desired polymerization temperature while the quench stream bypasses the heater and is injected into the catalyst bed as a cold stream. The feed
20 stream in either liquid or vapour form is introduced to the top of the catalytic reactor, which is filled with a catalyst consisting of a phosphoric acid film
25 adsorbed on an inert non-porous support. As desired, the disposition of catalyst within the reactor may be in the form of graduated and spaced beds or as a single solid bed. This latter type of reactor is
30 to be preferred, since it reduces the size of the reactor for a given catalyst volume and avoids the necessity of catalyst bed supports and the increased
35 difficulty in packing which are requisite when operating with an impregnated porous catalyst support.

The pressures maintained in the reactor are generally upward of about 150 psig
40 and the feed stream is introduced into the reactor at temperatures within the range of about 250 to 400° F. The particular optimum polymerization temperatures and pressures are dependent upon
45 the design of the system and especially the molecular weight and concentration of the olefins in the charge. A careful and critical control of temperatures within the catalyst bed are required to avoid
50 coke formation and excessive polymerization. For all practical purposes the catalyst temperatures should not exceed about 480° F. in order to minimize coking.

55 This temperature control is effected by the injection of cold feed or quench stream in a plurality of intermediate positions directly into the catalyst bed. The number of cold feed injections is
60 dependent upon the allowable temperature rise through the catalyst bed and the olefin concentration in the feed. In this respect, the subject film-acid catalyst allows a greater flexibility in temperature
65 variation than an impregnated

porous catalyst without noticeable effect on catalyst activity. As a general design criterion, the cold feed injection points are displaced so as to allow a maximum
70 of about 150° F. temperature rise through the catalyst bed or between injection points within the reactor.

In this type of operation, the olefin concentration is high at the inlet of the reactor and decreases progressively
75 throughout the reactor. The rate of reaction and, hence, the rate of heat evolution varies accordingly, so that for given temperature limits it is necessary to vary the bed size between the injection points
80 of the quench stream. The distance between injection points, or the depth of catalyst beds between injection points, will increase progressively throughout the reactor. The size of the various beds
85 between quench points will depend upon olefin concentrations of feed, olefin composition, and the allowable temperature rise. At these injection points, the cold feed is preferably injected directly into
90 the catalyst bed, such as by means of a distributor or spider embedded in the catalyst. In addition, the amount of quench stream supplied at each of the injection points required to keep the reactor
95 in heat balance will vary from point to point, and generally increases with the position of the injection point through the reactor. Furthermore, because of changes in reaction variables, such as
100 feed rate, feed composition, and catalytic activity, the distribution of quench stream to the various injection points will vary with time.

One of the added features of this process is an automatic control system which
105 operates to maintain a balance of temperature control throughout the catalytic reactor by controlling the quantities of cold feed to each of the injection
110 points. This control system is predicated upon the use of temperature controllers located within the reactor just before each of the quench points and at the outlet of the reactor. The amount of cold
115 feed injected at each of the quench points is controlled by the temperature controller just previous to the next quench point, and finally, the outlet of the reactor. This temperature controller is set for
120 the desired maximum catalyst temperature, which may range from about 370 to 450° F. Accordingly, the amount of feed passing through the preheater is that which is not taken up by the quench
125 streams, and thus, the distribution between preheated feed and cold quench feed will be varied automatically as necessary. For example, when the catalyst is active, the degree of conversion and, 130

BEST AVAILABLE COPY

hence, the amount of heat released, will be higher than normal, so that the total amount of quench required will be greater than normal; whereas, as the catalyst becomes spent, lesser amounts of the feed will be injected as quench streams and more will be preheated and passed through the entire reactor. Likewise, the distribution of quench to the various beds will be automatically varied with time; for example, with a fresh catalyst the amount of reaction occurring in the first few beds will be greater than normal. This requires that a greater proportion of the cold feed quench be distributed to the injection points at the inlets of these beds by the controllers in order to hold the temperature at the outlet of the beds at the prescribed maximum temperature. Later, as the top beds decline in activity, the amount of quench injection to the lower beds will be automatically increased.

By operating in this manner, charge stocks can be employed which contain a greater concentration of olefins than heretofore has been feasible. Whereas previously the maximum practical concentration of C_3 - C_4 olefins in the charge was about 35%, even when using stabilizer overhead as a recycle quench stream, the present process will permit concentrations of olefins up to about 49% when charging C_3 olefins and up to about 82% when charging C_4 olefins, with concentrations intermediate of these limits for the C_3 - C_4 olefin mixtures.

In order to exemplify the specific operation of the subject process and its preferred form and application, reference is made to the accompanying drawing and the following detailed description thereof. The specific embodiment described hereinafter is given by way of example and is not to be construed as a limitation either upon the particular apparatus or conditions employed, except as specifically indicated in the light of the previous disclosure.

The preferred feed introduced into the system through line 1 is a C_3 - C_4 olefin stream obtained from vapor recovery systems of conventional petroleum processing operations as, for example, a cracking operation. This feed is prepared for polymerization by subjecting it to a water wash in order to remove nitrogen compounds which are deleterious to a phosphoric acid catalyst. After water washing and settling, the feed stream temperature is normally around 80-100° F. and may be in a liquid or partial vapour state, depending upon the particular olefin concentrations, the amount of low molecular weight components in the

feed, and the pressure on the stream. Prior to introduction into the system, the feed stream is pressurized to substantially the operating pressure of the reactor, which, in this case, may range from 200-1000 psig, and preferably about 300 psig.

In this embodiment the pressurized water-washed feed stream is introduced at about 85° F. A portion of the feed stream passes through the heat exchanger 2, wherein the temperature of the feed is raised to about 300° F. by means of heat supplied from the neutralized polymerization product. The pre-heated feed at about 300° F. is introduced into the inlet of the reactor 4 through line 3. The reactor column 4 contains a solid bed of a phosphoric acid film catalyst and specifically a phosphoric acid film adsorbed upon an inert, non-porous support, such as quartz chips. These quartz chips are preferably of a 28-35 mesh size, and the concentration of the phosphoric acid film is at least 97%, and is preferably maintained at about 103-106%.

A second portion of the feed stream bypasses the heat exchanger through line 5 and is divided by suitable valves into the cold feed injection lines 6, 7, 8 and 9, which introduce the cold feed into the reactor 4 by means of the corresponding distributors 10, 11, 12 and 13. These distributors are located directly within the catalyst bed and may be in the form of any suitable means to effect the introduction of quench feed over as wide an area as possible. As previously noted, the number of cold feed injection points will vary with the size of the reactor, the olefin concentration of the feed, the desired average temperature in the beds, and the allowable temperature rise through the catalyst bed and/or between injection points. There are at least two injection points, and generally from 3 to 6 injection points necessary in the conventional polymerisation units of commercial size. For a feed containing about 44% mixed C_3 - C_4 olefins, three quench points will suffice to keep the reactor temperature between 300° F. and 400° F.

For normal operation, the preheated feed is introduced at about 300° F. and the allowable temperature rise between the injection points and through the catalyst bed is controlled to 100° F. Thus temperature is allowed to rise to about 400° F., at which point sufficient cold feed is introduced to quench back to 300° F. The distribution balance of preheated feed and cold feed quench to the various injection points, as well as the catalyst temperature control throughout the reactor, is attained by an automatic tempera-

BEST AVAILABLE COPY

ture control system actuated by the thermocouples 14, 15, 16, 17 and 18 displaced within the catalyst bed immediately preceding the four cold feed quench distributors and the outlet of the reactor. These thermocouples are connected to temperature controllers 19, 20, 21, 22 and 23, respectively, which automatically operate valves 24, 25, 26, 27 and 28, respectively.

As the preheated feed passes through the first catalyst bed, the desired temperature at the outlet of the first catalyst bed is controlled by thermocouple 14, which operates temperature controller 19, which in turn controls valve 24. This valve is placed in a bypass line 29, which shunts the preheater 2 as required to maintain the desired temperature at thermocouple 14. Particularly, when operating with a fresh catalyst charge, it may be necessary to lower the inlet temperature well below the normal of 300° F. and perhaps even as low as 250° F. in order to provide that the temperature at the thermocouple 14 does not exceed 400° F. The amount of cold feed quench injected through the distributor 10 at the top of the second bed is controlled by the outlet temperature of the bed at thermocouple 15 and its associated temperature controller 20. The temperature controller 20 is set to maintain the outlet temperature at 400° F. and controls the amount of cold feed quench by means of valve 25 in injection line 6. Each of the subsequent graduated beds is maintained in balance through its respective temperature controllers 21, 22 and 23. The control system maintains a uniform balance throughout the polymerization unit and is uniformly flexible to allow for any changes in olefin concentration of the feed and catalyst activity decline.

The volume of feed going through the preheater is that which is not taken up by the cold feed quench stream, and thus the distribution between preheated feed and cold feed quench is varied automatically as necessary. For example, when the catalyst is in a highly active state, the degree of conversion and, hence, the amount of heat released, will be higher than normal so that the total amount of quench injection required will be greater than normal; whereas, as the catalyst begins to decline in activity, less of the feed is injected as quench and greater amounts are preheated and passed through the entire reactor. Likewise, the distribution of cold feed quench to the various beds is varied automatically with time. For example, with a fresh catalyst, the amount of reaction occurring in the first beds will be greater than normal, which

requires that a greater proportion of cold feed quench be distributed to the inlets of these beds by the controllers in order to maintain a uniform outlet temperature of 400° F. Later, as the top beds decline in activity, the amount of quench to the subsequent beds will be automatically increased. The polymerized product consisting in this embodiment of the dimers and trimers is withdrawn from the reactor through line 30 and passes to a limestone neutralizer 31, wherein traces of entrained phosphoric acid are neutralized. The neutralized product then passes through line 32 into heat exchange with the incoming feed and thereafter to the recovery system.

The application of this cold feed injection to control the temperature in a polymerization process is critical to the use of a phosphoric acid film type of catalyst wherein the catalytic agent is adsorbed upon an inert, non-porous support. As previously noted and clearly evident, considerable amounts of cold feed are required to maintain a temperature balance on the system, particularly when using a feed containing high olefin concentrations. In order to maintain this temperature balance, it becomes necessary to inject sufficient cold feed quench to lower the temperature considerably below 300° F. The acid catalysts at temperatures below 300° F. absorb the water from the feed and become considerably diluted. When operating with the phosphoric acid film catalyst on a non-porous support, the only effect at these low temperatures would be a temporary reduction in activity, which aids in temperature control. However, when operating with an impregnated porous type of catalyst, the overhydration causes a softening of the catalyst pellets, with results crushing of the catalyst and plugging of the reactor.

The foregoing specific embodiment of the invention process has been described in connection with the production of polymers boiling within the gasoline boiling range. It is to be understood that the specific details described and shown in the drawing do not purport to illustrate all the processing and apparatus detail necessary in commercial operation and, accordingly, may be modified within the skill of the art for the specific type of installation desired.

It is to be understood that whilst reference has been made above to a "cold" olefinic charge, this term has only been used in a relative fashion to distinguish from the preheated charge. The "cold" charge may itself be at an elevated temperature which is, of course, below that of the preheated charge.

BEST AVAILABLE COPY

What we claim is:—

1. A process for producing polymers of normally gaseous olefin hydrocarbons which comprises passing a preheated charge of said olefins through a catalytic reaction zone wherein the catalyst consists of a film of phosphoric acid adsorbed on a non-porous, inert support maintained under polymerizing conditions, introducing an olefinic charge having a temperature below that of the preheated charge at a plurality of intermediate positions within said catalytic reaction zone and controlling the polymerization reaction temperature throughout the catalyst zone by the injection of controlled quantities of said olefinic charge at each of the intermediate injected positions.
2. A process as claimed in claim 1, wherein the flow of olefinic charge to each of the intermediate positions within said catalytic reaction zone is automatically controlled by temperature controllers actuated by temperature-measuring devices dispersed within the catalyst zone.
3. A process as claimed in claim 1 or 2, wherein the olefinic charges contain at least 35% of said olefins.
4. A process as claimed in claim 1 or 2, wherein the olefinic charges are water-

washed prior to their passage through the catalytic reaction zone.

5. A process as claimed in any preceding claim, wherein the preheated charge is heated to a temperature substantially 35 within the range 250° to 400° F. and the polymerization is effected in a catalytic reactor at a pressure greater than 150 psig, the injection of controlled quantities of olefinic charge being controlled so as to allow a maximum of about 150° F. temperature rise between injection points within the reactor and the outlet of the reactor.

6. A process for producing polymers of normally gaseous olefin hydrocarbons substantially as hereinbefore described, with reference to the accompanying drawing.

7. Polymers of normally gaseous olefin hydrocarbons when produced by the process claimed in any of the preceding claims.

Dated the 9th day of March, 1951.
HASELTINE, LAKE & CO.,
28, Southampton Buildings,
London, W.C.2, and
19/25, West 44th Street,
New York, U.S.A.,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

BEST AVAILABLE COPY

***This drawing is a reproduction of
the Original on a reduced scale.***

